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Processing and Properties of Fiber Reinforced Polymeric Matrix Composites: I. IM7/LARCTM-PETI-7 Polyimide Composites

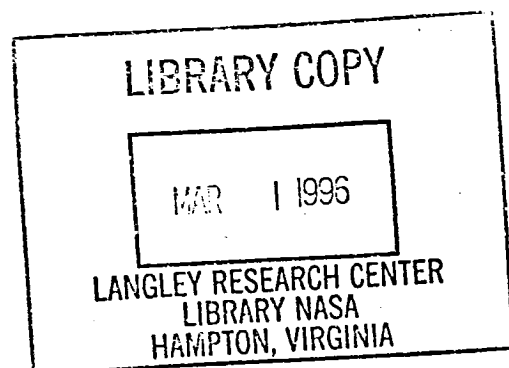
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STATEMENT OF WORK

LARC™-PETI-7 (LAnglely Research Center™-PhenylEthynyl Terminated Imide-7) is a new polyimide invented by Dr. T. L. St. Clair of the Composites and Polymers Branch, NASA Langley Research Center. The objective of this work was to develop a molding cycle and to evaluate the mechanical properties of IM7/LARC™-PETI-7 composites. The following tasks were included in this investigation:

- i) Characterizing thermal and rheological properties of the matrix resin.
- ii) Designing a workable molding cycle for the laminate fabrication.
- iii) Evaluating the composite mechanical properties.

Processing and Properties of Fiber Reinforced Polymeric Matrix Composites:
I. IM7/LARC™-PETI-7 Polyimide Composite*

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1. ABSTRACT

A phenylethynyl terminated imide oligomer formed from the reaction of benzophenone tetracarboxylic acid dianhydride, an 75:25 molar ratio of 4,4'-oxydianiline and meta-phenylenediamine and 4-phenylethynylphthalic anhydride as the endcapper at a theoretical number average molecular weight (M_n) of ~ 3,700 g/mol was evaluated as a composite resin matrix. A glass transition temperature (T_g) of 315°C was reached after 250°C/1 hr annealing of the matrix resin. Unidirectional prepreg was made by coating an N-methylpyrrolidinone solution of the amide acid oligomer onto unsized IM7 graphite fibers. The thermal and rheological properties and the solvent/volatile depletion rates of the amide acid/NMP system were determined. This information was used to successfully design a molding cycle for composite fabrication. Composites molded under 800 Psi at 371°C consistently yielded good consolidation as measured by C-scan and optical photomicrography. The composite's short beam shear strength (SBS), longitudinal and transverse flexural strengths and moduli were measured at various temperatures. These composites exhibited excellent room temperature (RT) longitudinal flexural strength and modulus and RT SBS strength retention at 177°C.

KEY WORDS LARC™-PETI-7, Poly(amide acid), Thermoplastic Polyimides, Carbon Fiber, Composite, Molding Cycle, Mechanical Properties.

*This work was performed at NASA Langley Research Center, Hampton, Virginia.

2. EXPERIMENTAL*

2.1 LARC™-PETI-7 Poly(amide acid)/NMP Solution

The 30% w/w LARC™-PETI-7 Poly(amide acid)/NMP solution was manufactured by Imitec Inc. (Schenectady, NY). This concentrated solution was used as received.

2.2 Thermogravimetric Analyzer (TGA)

The residual solvent/volatile content in the matrix resin was measured by a Seiko TG/DTA 220 thermogravimetric analyzer (TGA) at 2.5°C/min in flowing (40mL/min) air.

2.3 Differential Scanning Calorimetry (DSC)

A Shimadzu DSC-50 calorimeter was used to study T_g shifts and crystallization kinetics for the as-prepregged neat resin at 20°C/min.. Resin was annealed in the DSC to generate various degrees of crystallinity. The T_g was taken at the inflection point of the endotherm; the peak melting temperature (T_m) and the heat of fusion (ΔH) were taken from the crystalline melt endotherm.

2.4 Melt Rheology

Rheological measurements were conducted on a Rheometrics System 4 rheometer. Sample prepreg specimens were prepared with dimensions 2.5" x 0.5". Five to six layers of prepreg were stacked to reach a required thickness of approximately 0.060" for measurement. The torsional rectangular mode was used in the rheometer. The top end of the specimen was oscillated at a fixed strain of 0.1%, and a fixed angular frequency of 10 rad/sec, while the lower plate was attached to a transducer which recorded the resultant torque. Storage (G') and loss (G'') moduli were measured as a function of time (t) at several designed temperature profiles. These moduli were then converted to the complex viscosity $\eta^*(t)$.

*Use of trade names or manufacturers does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.

2.5 Composite Mechanical Properties

Unidirectional prepreg was fabricated on a multi-purpose tape machine [1] using the 30% w/w oligomeric amide acid solutions in NMP. Composite mechanical properties including SBS strength (ASTM D2344), longitudinal and transverse flexural strength and modulus (ASTM D790) were measured at RT and elevated temperatures. The molding cycle for the composites was restricted to temperatures $\leq 371^{\circ}\text{C}$ (700°F). Values for resin and void contents were determined by acid digestion in which 1:1 w/w concentrated sulfuric acid and 30 percent hydrogen peroxide were used. The calculations were based on a density of $1.77 \times 10^3 \text{ Kg/m}^3$ (1.77 g/cc) for the IM7 fiber and 1.3 Kg/m^3 (1.3 g/cc) for the cured LARCTM-PETI-7 resin.

3. RESULTS AND DISCUSSION

3.1 Solvent/Volatile Depletion Behavior

As described earlier, the unidirectional prepreg was manufactured by impregnating carbon fibers with 30% w/w oligomeric amide acid/NMP solution. The synthetic scheme is depicted in Figure 1. Imidization is a condensation reaction which in this case releases H₂O as a by-product. A thorough understanding of the solvent and volatile depletion behavior from the composite laminate has been shown to be critically important in the design of a successful molding cycle for a given fiber/resin composite system [2-6].

Weight loss behavior was measured by TGA on resin specimens which were taken from the prepreg flash. Therefore, neat resin with thermal history identical to the prepreg was studied for the solvent/volatile depletion behavior. Specimens were exposed to various thermal treatments in an open pan in the DSC. The TGA weight loss profiles and results are shown in Figure 2 and Table 1, respectively.

The weight loss profiles for all specimens exhibited a common two-step characteristic: the lower temperature (approximately 120 to 225°C) weight loss is primarily due to the loss of NMP and H₂O while a higher temperature (above 450°C) weight loss is due to the degradation of the cured polymer. Therefore, the first steep weight loss in the TGA profile indicates the amount of volatiles in each specimen after the initial thermal treatment defined in Table 1. As the treatment temperatures increased, the weight loss onset temperatures also increased while the residual volatile weight fractions within the specimens decreased. The weight loss onset temperatures were estimated to be 5 to 25°C higher than the treatment temperatures. A 23% w/w volatile content was found for the as-prepregged resin flash. The amount of volatiles decreased rapidly at the higher treatment temperatures. Less than 0.5% residual volatiles remained after exposure at 250°C for 1 hr. The volatile content in the as-prepregged resin flash was based on the weight of neat resin only. The prepreg (fiber + resin) exhibited a residual volatile content of about 15%.

The resin's T_g , crystal melting temperature (T_m) and heat of fusion (ΔH) are also tabulated in Table 1 for those specimens prepared for the TGA measurements. The effect of these weight losses in the molding cycle design will be discussed below.

3.2 Thermal Properties

The crystallization and imidization behavior of the LARCTM-PETI-7 neat resin was investigated by DSC. In order to preserve the thermal history experienced during the prepregging operation, resin specimens were taken directly from prepreg flash. A previous investigation conducted directly on the IM7/PETI prepreg [5] revealed that similar behavior was observed. The results reported below should be applicable to the composite laminate during fabrication.

The as-prepregged material was wet (contained ~15% volatiles including NMP) and no T_g was detected. In an effort to design a workable molding cycle, the imidization and crystallization behavior of the as-prepregged resin annealed at various temperatures was investigated by DSC. The resulting thermograms are shown in Figure 3. Two annealing conditions performed prior to the scans are indicated.

T_g , T_m and ΔH are tabulated in Table 1. The DSC thermograms indicate that initial T_g values were not detectable regardless of the specimen's thermal pre-treatment. Values of T_g were measured from the second temperature scan immediately following the first scan shown in Figure 3. The T_g increased with higher annealing temperature. The highest T_g ($= 315^\circ\text{C}$, Table 1) was obtained for a specimen annealed at 250°C for 1 hr.

Two melting endotherms were clearly evident for both as-prepregged and as-annealed specimens. T_m is equal to 344°C and 373°C for the lower and higher melting peak temperature, respectively. Values of ΔH were small (approximately 5 J/g). It was evident that both the T_m and ΔH were not affected by the thermal pre-treatment conditions.

Each specimen became totally amorphous after heating to 400°C . In fact, after the initial melt, the crystallinity in LARCTM-PETI-7 could not be re-generated under any annealing conditions. The high T_g (315°C) combined with the high T_m (375°C) that resulted from the $250^\circ\text{C}/1$ hr annealing suggested that the processability of LARCTM-PETI-7 will be poor under moderate temperatures (i.e., 371°C) and pressures (i.e., 200 Psi). The effect of these thermal properties in the molding cycle design will be discussed later.

3.3 Rheological Properties

Complex viscosity, $\eta^*(t)$, was measured on IM7/LARC™-PETI-7 composite. A temperature profile simulating a composite molding cycle was followed. The two step profile consisted of

1. Ramp at 4°C/min from RT to 250°C and hold for 1 hr.
2. Ramp at 4°C/min from 250 to 371°C and hold for 1 hr.

The results of the rheological investigation are shown in Figure 4. Also included in the Figure is the $\eta^*(t)$ of IM7/LARC™-PETI-5 composite following the same temperature profile [6]. Initial drops in the $\eta^*(t)$ values during the temperature heat-up were attributed to matrix softening. At 150° - 175°C, values of $\eta^*(t)$ reached a minimum and started to rise with the temperatures indicating the commencement of the imidization reaction within the matrix resin. The rate of increase of $\eta^*(t)$ diminished gradually at 250°C suggesting a near completion of imidization reaction at the end of 1 hr hold.

The $\eta^*(t)$ dropped monotonically during the second ramp from 250 to 371°C. For IM7/LARC™-PETI-5 composite, two reflection points in $\eta^*(t)$ profile located near 290°C and 350°C were evident. These inflection points corresponded to the two endothermic peaks observed for the resin subjected to a 250°C/1 hr annealing [6]. On the other hand, only a single inflection point located near 310°C was recorded in the $\eta^*(t)$ profile for IM7/LARC™-PETI-7 composite. This inflection point corresponded to the T_g of the LARC™-PETI-7 matrix resin which was measured to be 315°C (see Table 1). Unlike IM7/LARC™-PETI-5 composite, the T_m s were not detectable in the $\eta^*(t)$ profile due to small quantity of endothermic ΔH found in the LARC™-PETI-7 resin (see Table 1).

The minimum η^* was reached at 371°C for both composites. During the 371°C hold, crosslinking reactions were triggered and the resin matrices were transformed quickly to viscoelastic solid-like form with increasing η^* .

Due to the presence of the fibers (approximately 70% w/w) in the prepreg specimens, the rates of increase in $\eta^*(t)$ profiles, due to crosslinking reactions, during the 371°C hold were much smaller than those measured for the neat resin specimens [6]. The $\eta^*(t)$ profile suggests that pressure for IM7/LARC™-PETI-7 laminate fabrication should be applied shortly after the 250°C/1 hr hold to obtain maximum benefit of the melt fluidity. This melt fluidity increases as the temperature approaching 371°C. After holding at 371°C, η^* increases due to reaction of the phenylethynyl groups. A hold at 250°C/1 hr permits most of the volatiles to escape leaving residual volatiles of < 0.5% (Figure 2 and Table 1).

3.4 Composite Molding Cycle

In order to attain a void-free composite, solvent and reaction by-products must be eliminated before applying pressure. However, for the LARC™-PETI-7 fully imidized resin which exhibited poor procesability (i.e, high T_g and T_m as discussed above), a processing window (temperature and pressure profiles) must be identified. This will take full advantage of the small amounts of residual volatiles that may provide a plasticizing effect on the resin [2,3].

As-prepregged IM7/LARC™-PETI-7 prepreg was first dried (i.e., B-staging) in a forced air circulation oven. Oven (B-staging) temperatures of 180°C, 200°C and 225°C were selected. After 1 hr B-staging in oven, the prepreg was trimmed and stacked in the mold and placed in a press for consolidation. Three 3" x 3" - [0]₂₄ laminates were fabricated. Their C-scan images were shown in Figure 5. Consolidating temperature of 371°C was held for 1 hr. A pressure of 500 or 800 Psi was applied from RT and held throughout the cycle.

The C-scan patterns in Figure 5 were closely relatable to the residual solvent/volatile contents measured in Table 1. A 6.5% w/w residual volatile was measured for matrix resin subjected to 180°C/1 hr B-staging (Table 1). This volatile level offered desired resin fluidities that enable resin infiltration within the composite during consolidation. However, excessive residual reactions apparently occurred during the 371°C/1 hr hold. The reaction by-products (i.e., water) were trapped inside the laminate because the consolidating pressure effectively blocked all the volatiles' escape passages. This resulted to a C-scan pattern which revealed a voidy area in the center of the 180°C/1 hr B-staged laminate (Figure 5(a)).

Raising the B-staging temperatures lowered the residual volatiles content. A 2% w/w residual volatile existed in matrix resin subjected to 225°C/1 hr B-staging (see Table 1). The center area of the laminate was no longer voidy as shown in the C-scan image (Figure 5(c)). However, in this situation lower fluidities resulted due to the higher degree of imidization for the resin matrix. 500 Psi was seen insufficient to squeeze out excess resin and the laminate was voidy along its peripheral area. While the B-staging condition remained the same (i.e., 225°C/1 hr), the laminate consolidation quality was greatly improved using 800 Psi (Figure 5(d)). Residual volatile content could be reduced to < 0.5% w/w when subjected to 250°C/1 hr B-staging (see Table 1). However, higher pressure was required for consolidation because of poorer fluidity asociated with an even higher degree of imidization.

The molding cycle developed for fabricating IM7/LARC™-PETI-7 laminate as shown in Figure 6 consisted of the following steps:

- 1) B-stage prepreg 225°C for 1 hr in oven.
- 2) Apply 800 Psi from RT while increasing temperature at ~3°C/min to 371°C and hold for 1 hr.
- 3) Cool in press. Release pressure below 100°C.

This cycle consistently yielded well-consolidated IM7/LARC™-PETI-7 laminate that showed no voids by ultrasonic C-scan or optical photomicrography.

3.5 Composite Mechanical Properties

Mechanical properties such as SBS strength, longitudinal and transverse flexural strengths and moduli were determined for the IM7/LARC™-PETI-7 composites. Laminate stacking sequence, specimen size and quantity, test temperatures and resin content for the composites used in these tests are summarized in Table 2. Resin contents varied from 27.2 to 32.1% by weight. The composites were well-consolidated as evidenced from C-scan and optical microscopy. They also contained low void content as determined by acid digestion.

SBS strengths and flexural strengths and moduli were measured at RT, 150°, and 177°C. These results are tabulated in Table 3. SBS strength values were moderate with IM7 fiber. Near 80% RT strength retention at 177°C was excellent.

A very decent flexural strength was obtained at RT. The strength value at 177°C was, however, a little low. Flexural moduli were very good at all temperatures.

The transverse flexural data is often used as a barometer of resin/fiber adhesion. This value at RT was about half of IM7/LARC™-IA composite [5], but comparable to IM7/LARC™-ITPI composite [2], a reflection of poor processability. This strength value could be improved by using higher consolidation pressures.

4. CONCLUSIONS

Rheological behavior, volatile depletion rate and the thermally induced crystallization of LARC™-PETI-7 were determined and used to develop fabrication conditions for void-free composites. After 1 hr at 225°C, T_g reached 306°C, and the prepreg volatile content was reduced to < 2% w/w. This residual volatile level offered the desired plastisizing effect that enhanced fluidity of the imidized resin matrix enabling laminate consolidation at 371°C and 800Psi.

Composites fabricated for 1 hr at 371°C under 800 Psi gave well-consolidated panels. The composites exhibited moderate RT SBS strength but excellent strength retention at 177°C. Very decent longitudinal flexural strength and modulus were obtained. The transverse flexural properties were poorer and could be improved through the use of higher consolidation pressures.

5. REFERENCES

1. S. P. Wilkinson, J. M. Marchello, D. Dixon and N. J. Johnston, "A New NASA LaRC Multi-purpose Prepregging Unit", *Sci. Adv. Matl. Proc. Engr. Ser.*, **38**, 1 (1993)
2. T. H. Hou, E. J. Siochi, N. J. Johnston and T. L. St. Clair, "IM7/LARC™-ITPI Polyimide Composites", *Polymer*, **35** (23), pp. 4956-4969, November 1994
3. T. H. Hou, S. P. Wilkinson and B. J. Jensen, "Processing and Properties of IM7/LARC™-8515 Composite". to appear in *Polyimides - Materials, Chemistry and Characterization - V*, Ed. C. Feger, M. M. Khojasteh, and J. E. McGrath, Elsevier Sci. Publishers B.V., Amsterdam, 1995
4. B. J. Jensen, T. H. Hou and S. P. Wilkinson, "Adhesive and Composite Properties of LARC™-8515 Polyimide", *High Perform. Polym.*, **7**, 11-21 (1995)
5. T. H. Hou, N. J. Johnston and T. L. St. Clair, "IM7/LARC™-IA Polyimide Composites", *High Perform. Polym.*, **7**, 105-124, 1995
6. T. H. Hou, B. J. Jensen and P. M. Hergenrother, "Processing and Properties of IM7/PETI Composites", to appear in *J. Comp. Matl.*, 1995

Table 1. Weight loss behavior of LARC™-PETI-7/NMP Poly(amide acid)*

Thermal Treatment	¹ Weight Loss		Thermal Property		
	Onset temperature (°C)	Residual solvent weight fraction (%)	T _m (°C)	² T _g (°C)	ΔH (J/g)
As-prepregged	100	23	375	281	4.1
180°C/1hr	190	6.5	---	---	---
200°C/1hr	225	3.5	---	---	---
225°C/1hr	230	2	373	306	4.6
250°C/1hr	275	< 0.5	372	315	5.0

*Measurements were made on resin flash collected from IM7/LARC™-PETI-7 prepregs (TM-105) as manufactured from 30% solids amide acid solution in NMP using a multi-purpose tape machine.

¹Measured by TGA.

²T_g values were measured on these thermally treated resin specimen after an additional temperature scan at 20°C/min from RT to 400°C and cool

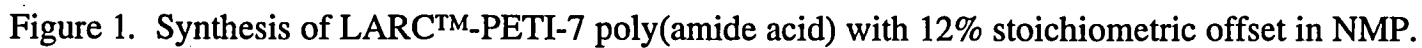
Table 2. Mechanical Tests For IM7/LARC™-PETI-7 Polyimide Composites

Mechanical Test	Laminate lay-up	Length (in)	Width (in)	Meas. temp., °C	Quantity at each temp.	% Content		
						Resin w/w	Resin v/v	Void v/v
SBS	[0] ₂₀	0.75	0.25	RT, 150, 177	6-7	28.17	34.36	1.29
0° Flexural	[0] ₁₀	2.75	0.5	RT, 150, 177	3-4	27.21	33.24	1.44
90° Flexural	[0] ₁₀	1.0	0.5	RT, 150, 177	3-4	32.07	39.10	0.1

Table 3. Mechanical Properties of IM7/LARC™-PETI-7 Composites

Mechanical Properties	Temperature, °C	IM7/LARC™-PETI-7 (3,700 g/mol)
SBS Strength, Ksi	RT	9.64
	150	7.93
	177	7.53
0° Flexural Strength, Ksi	RT	248.0
	150	195.0
	177	181.8
0° Flexural Modulus, Msi	RT	21.3
	150	21.2
	177	20.9
90° Flexural Strength, Ksi	RT	12.2
	150	9.1
	177	8.9
90° Flexural Modulus, Msi	RT	.54
	150	.43
	177	.45

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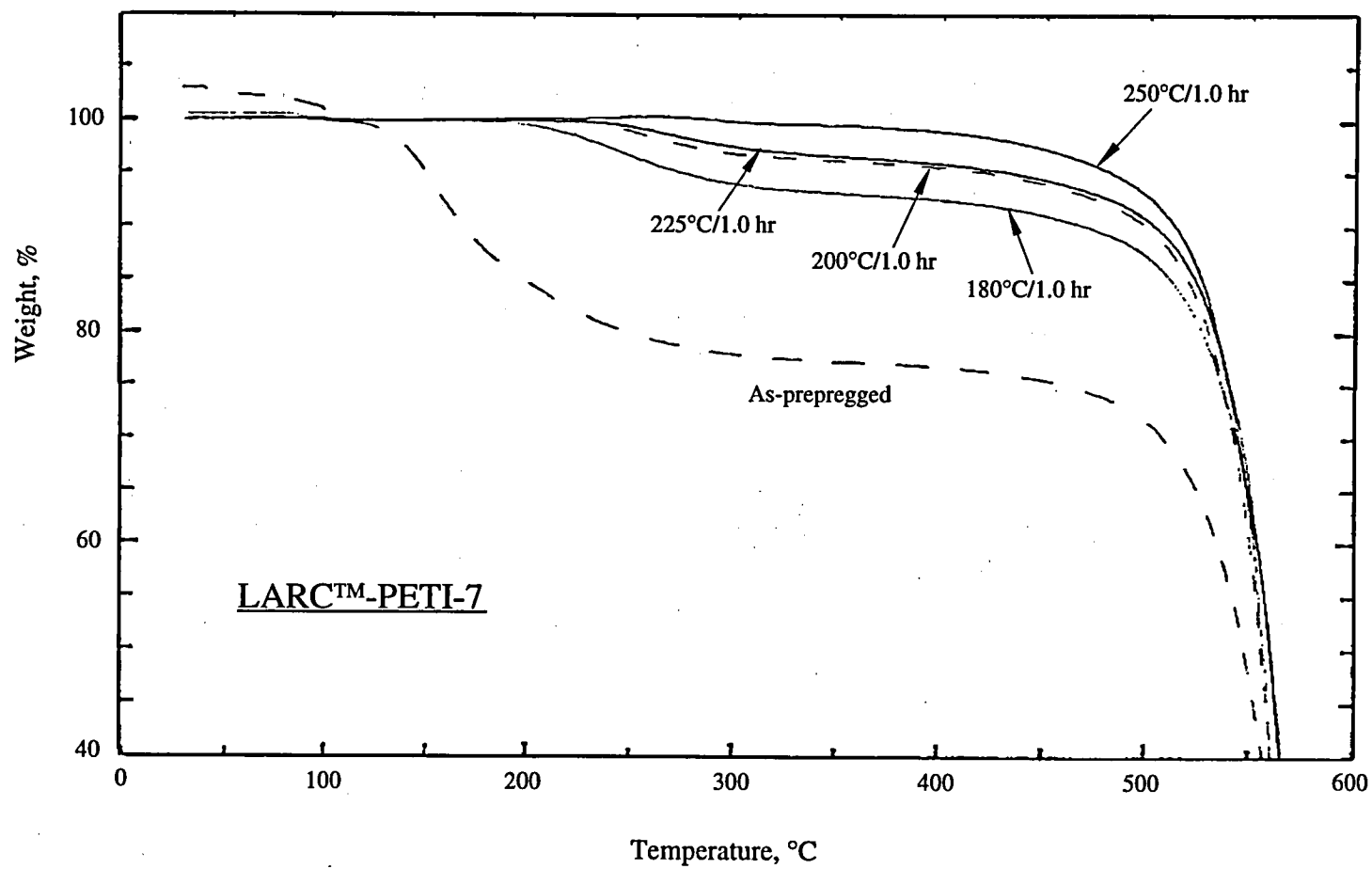


Figure 2. TGA weight loss profiles of IM7/LARC™-PETI-7 resin pre-cured under various thermal conditions.

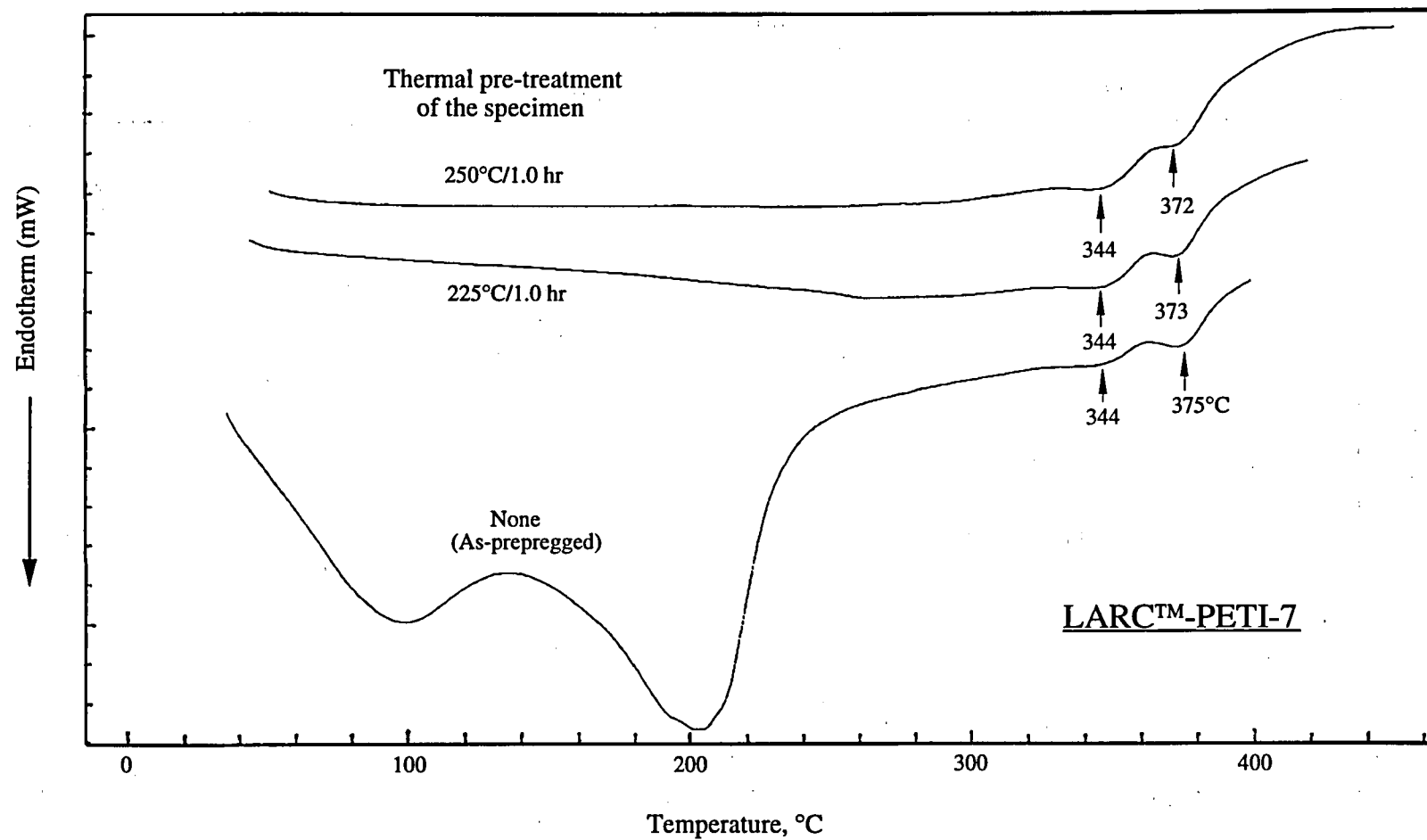


Figure 3. DSC thermograms of LARC™-PETI-7 neat resin.

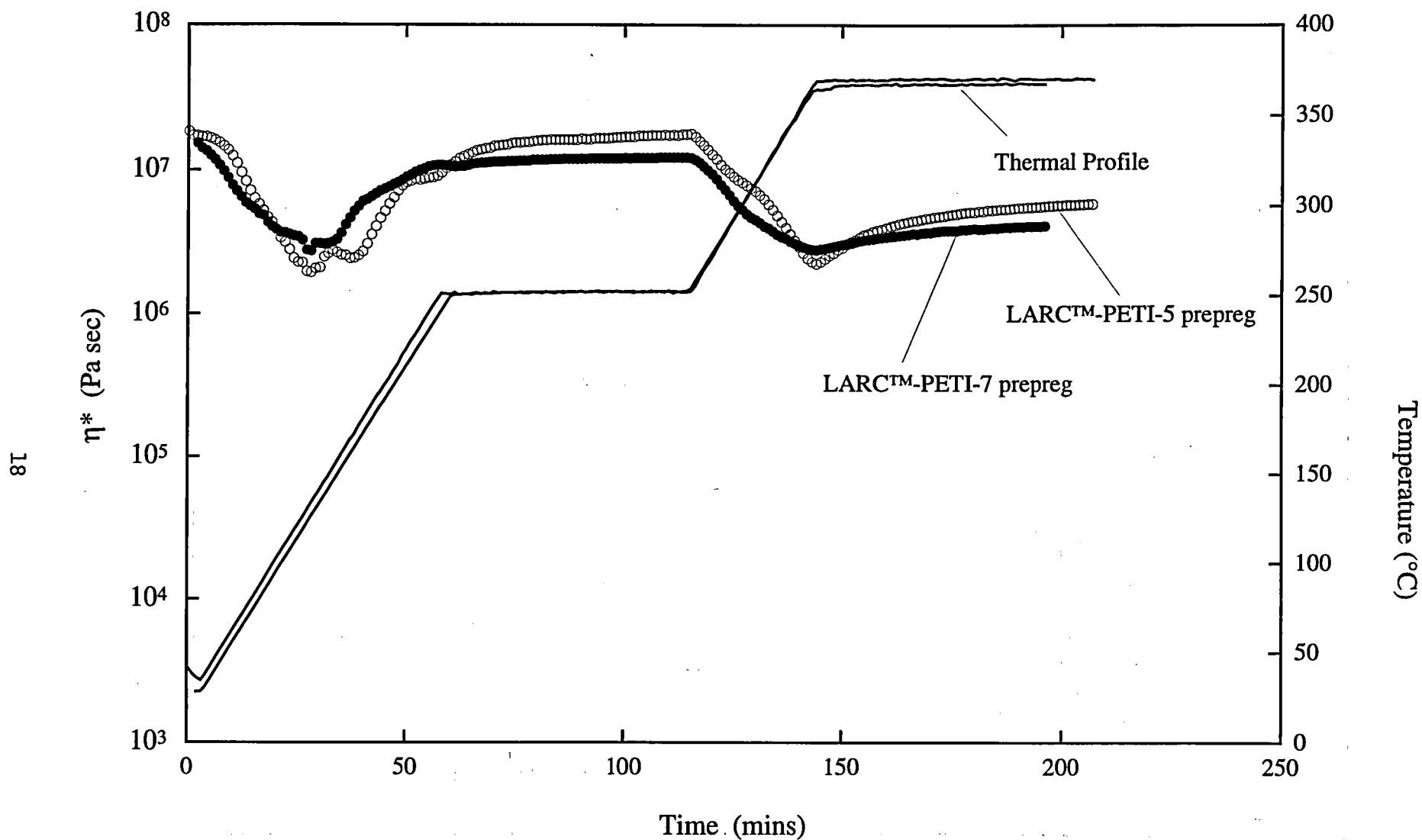
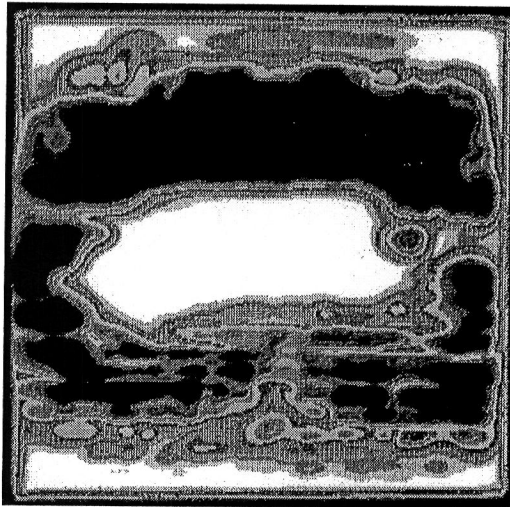


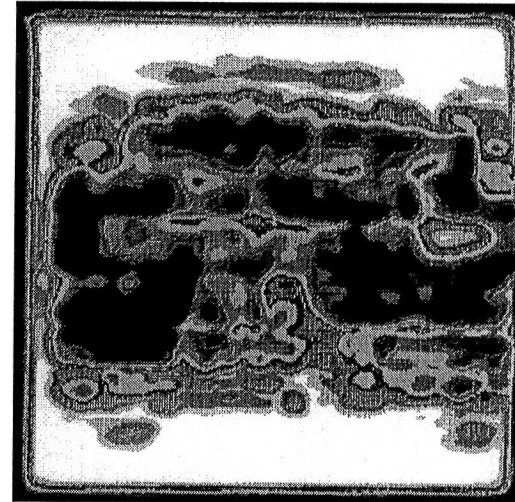
Figure 4. Complex viscosity (η^*) as a function of time for two IM7/PETI preregs.

IM7/LARC™-PETI-7 Laminates

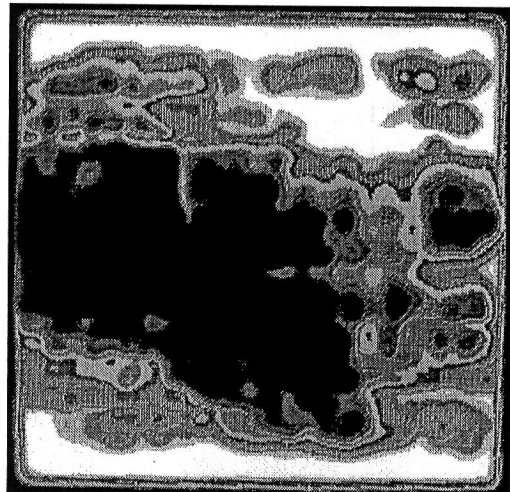
[0]₂₄ - 3" x 3"



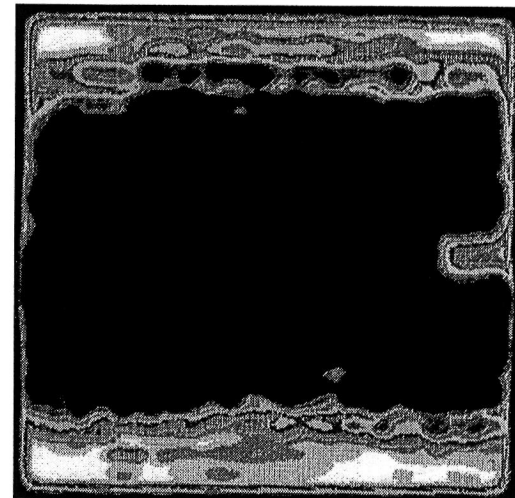
(a) 180°C/1 h 500 psi



(b) 200°C/1 h 500 psi



(c) 225°C/1 h 500 psi



(d) 225°C/1 h 800 psi

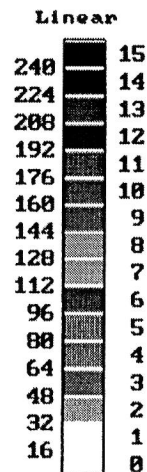


Figure 5. C-scan images for PETI-7 laminate panels molded under various conditions.

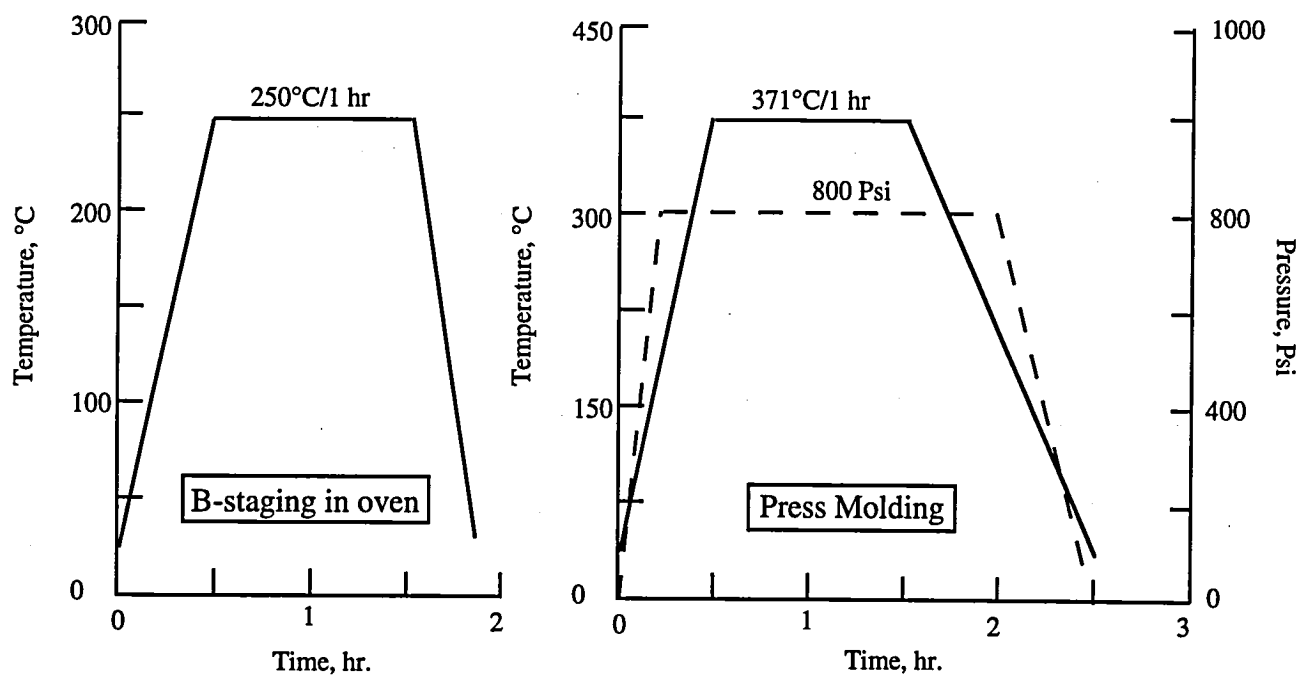


Figure 6. Molding cycle for IM7/LARC™-PETI-7 composite.

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